

Elastic properties of quaternary oxyarsenide LaOFeAs as basic phase for new 26-52K superconductors

I.R. Shein* and A.L. Ivanovskii

Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, 620219, Ekaterinburg, Russia

The full-potential linearized augmented plane wave (FP-LAPW) method with the generalized gradient approximation (GGA) for the exchange-correlation potential has been applied to predict the elastic properties of quaternary oxyarsenide LaOFeAs - the basic phase for the newly discovered 26-52K superconductors. The optimized lattice parameters, independent elastic constants (C_{ij}), bulk modulus B , compressibility β , and shear modulus G are evaluated and discussed. For the first time the numerical estimates of the elastic parameters for polycrystalline LaOFeAs ceramics are performed. Our analysis shows that LaOFeAs belong to the anisotropic mechanically stable systems; a parameter limiting the mechanical stability of this material is the shear modulus. In addition, LaOFeAs is a soft material ($B \sim 98$ GPa) with high compressibility ($\beta \sim 0.0102$ 1/GPa); lays at the border of a brittle behavior and adopts a high ionic contribution in intra-atomic bonding.

* E-mail: shein@ihim.uran.ru

The elastic properties are of great importance for the material science of superconductors; on the other hand, the elastic constants can be linked to such important physical parameters of superconductors, as the Debye temperature Θ_D and the electron-phonon coupling constant λ [1]. In the past years, the elastic properties of various superconducting materials have been studied extensively, and some correlations between the superconducting critical temperature T_c and mechanical parameters have been discussed. So, Hirsh [2] has suggested that high T_c s are associated with low values of the bulk modulus B , i.e. high compressibility β . Really, for the many groups of superconductors with enhanced critical temperatures (such as YBCO, MgB₂, MgCNi₃, boride-carbides and carbide-halides of the rare earth metals, REM₂B₂C and RE₂C₂X₂ etc) their bulk modulus does not exceed $B \leq 200$ GPa ($\beta \geq 0.005$ 1/GPa) [1, 2, 3, 4, 5, 6, 7]. On the other hand, the superconducting transition (up to $T_c \sim 11$ K) was found for such hard and incompressible material as boron-doped diamond [8, 9].

Except scientific interest, mechanical properties appear extremely important for technology and various advanced applications of superconducting materials [10].

In February 2008 the new layered superconductor: electron doped quaternary oxyarsenide LaOFeAs (LaO_{1-x}F_xFeAs, $x \sim 0.05-0.12$) with T_c at about 26K was reported [11], and this surprising discovery has stimulated much activity for search of the new superconducting materials based on this phase. It was found that also hole-doped oxyarsenide LaOFeAs (La_{1-x}Sr_xFeAs, by partial substitution of La by Sr) adopts superconductivity with T_c at about 25K [12]. Moreover by replacing of La by others rare earth elements it seems to be possible to achieve the further enhancing of T_c (41K - for CeO_{1-x}F_xFeAs [13], 43K - for SmO_{1-x}F_xFeAs [14], 50-52K - for PrO_{1-x}F_xFeAs and NdO_{1-x}F_xFeAs [15, 16]).

Alongside with the intense efforts in synthesis of new doped quaternary oxypnictides and examining of su-

perconductivity parameters, some of their physical properties have been investigated. So, today the interplay between superconductivity and spin fluctuations, band structure, Fermi surface, and phonon spectra for some quaternary oxypnictides are discussed at the theoretical level [17, 18, 19, 20, 21, 22, 23, 24]; the photoemission spectra of SmO_{0.85}F_{0.15}FeAs are obtained [25] and pressure experiments for LaO_{1-x}F_xFeAs ($x=0.11$) are performed [26].

In this Report we focus on the elastic properties of monocrystalline quaternary oxyarsenide LaOFeAs as the basic phase for the newly discovered 26-52K superconductors. In addition the numerical estimates of the elastic parameters of the polycrystalline LaOFeAs ceramics, which may be important for the future applications of new superconducting materials are performed for the first time.

The oxyarsenide LaOFeAs has a tetragonal (ZrCuSiAs-type structure, space group P4/nmm[27]) layered structure, where Fe atoms are arrayed on a square lattice in the form of edge-shared tetrahedra FeAs₄. Each (Fe-As)⁻ layer is sandwiched between (La-O)⁺ layers.

Our calculations based on density functional theory (DFT) with generalized gradient approximation (GGA) in PBE form [28] for the exchange-correlation potential and were performed by means of the full potential method with mixed basis APW+lo (LAPW) implemented in the WIEN2k suite of programs [29]. The calculations are performed with full lattice optimizations (lattice parameters and atomic coordinates); the self-consistent calculations were considered to be converged when the difference in the total energy of the crystal did not exceed 0.001 mRy as calculated at consecutive steps, and the nonmagnetic state was treated. Other details are described in Ref [6].

Firstly, the equilibrium lattice constants (a and c) were evaluated - in reasonable agreement with available data, Table I.

Secondly, the values of six independent elastic constants

TABLE I: Calculated lattice constants (a, c, in Å), cell volume (Vo, in Å³) elastic constants (C_{ij}, in GPa), bulk modulus (B, in GPa), shear modulus (G, in GPa) and B/G ratio for tetragonal monocrystalline LaOFeAs as well as some elastic parameters for polycrystalline LaOFeAs ceramics as obtained in the Voigt-Reuss-Hill approximation: bulk modulus (B_{VRH}, in GPa), compressibility (β_{VRH}, in GPa⁻¹), shear modulus (G_{VRH}, in GPa), Youngs modulus (Y_{VRH}, in GPa) and Poissons ratio (ν).

a	4.033 (4.036 [11]; 4.037 [30]) ^a	B _V (B _R) ^b	98.5 (97.2)
c	8.684 (8.739 [11]; 8.629 [30]) ^a	G _V (G _R) ^b	56.5 (55.9)
V ₀	141.2	B _V /G _V	1.74
C ₁₁	191.9	B _{VRH}	97.9
C ₁₂	55.9	β _{VRH}	0.01022
C ₁₃	61.6	G _{VRH}	56.2
C ₃₃	144.8	Y _{VRH}	141.5
C ₄₄	44.1	ν	0.259
C ₆₆	77.9		

^a in parentheses the available experimental (Ref.[11]) and calculated (Ref.[30]) data are given

^b in Voigt (and Reuss) approximations

(C_{ij}; namely C₁₁, C₁₂, C₁₃, C₃₃, C₄₄ and C₆₆) for LaOFeAs were estimated by calculating the stress tensors on applying different deformations given on the equilibrium lattice of tetragonal unit cell and determining the dependence of the resulting change in energy on the deformation, Table I. All these elastic constants are positive and satisfy the well-known Born's criteria for mechanically stable tetragonal crystal: C₁₁ > 0, C₃₃ > 0, C₄₄ > 0, C₆₆ > 0, (C₁₁ - C₁₂) > 0, (C₁₁ + C₃₃ - 2C₁₃) > 0 and 2(C₁₁ + C₁₂) + C₃₃ + 4C₁₃ > 0. The calculated anisotropic factor A = 2C₄₄/(C₁₁-C₁₂) is 0.65, i.e. LaOFeAs phase is mechanically anisotropic, because a value of A = 1 represents completely elastic isotropy, while values smaller or greater than 1 measure the degree of elastic anisotropy.

The calculated elastic constants allow us to obtain the macroscopic mechanical parameters of LaOFeAs, namely bulk modulus (B) and shear modulus (G) - in two main approximations: Voigt (V) [31] and Reuss (R) [32], in the following forms:

$$B_V = \frac{1}{9}\{2(C_{11} + C_{12}) + C_{33} + 4C_{13}\}$$

$$G_V = \frac{1}{30}\{M + 3C_{11} - 3C_{12} + 12C_{44} + 6C_{66}\}$$

$$B_R = \frac{C^2}{M}$$

$$G_R = 15\left\{\frac{18B_V}{C^2} + \frac{6}{C_{11} - C_{12}} + \frac{6}{C_{44}} + \frac{3}{C_{66}}\right\}^{-1}$$

where C² = (C₁₁ + C₁₂)C₃₃ - 2C₁₃ and M = C₁₁ + C₁₂ + 2C₃₃ - 4C₁₃. The results obtained are summarized in Table I.

Next, as LaOFeAs samples are usually prepared and investigated as polycrystalline ceramics [11,12,25,26] in the form of aggregated mixtures of microcrystallites with a random orientation, it is useful to estimate the corresponding parameters for the polycrystalline material from the elastic constants of the single crystal. To this aim we utilize the Voigt-Reuss-Hill (VRH) approximation. In this approach, according to Hill[33], the Voigt and Reuss averages are limits and the actual effective modules for polycrystals could be approximated by the arithmetic mean of these two bounds. Then, one can calculate the averaged compressibility (β_{VRH} = 1/B_{VRH}), Young modulus (Y_{VRH}) and from the B_{VRH}, G_{VRH} and Y_{VRH} one can evaluate the Poissons ratio (ν). All these parameters are also listed in Table I. Certainly all of these estimations are performed in limit of zero porosity of LaOFeAs ceramics.

From our results we see that for LaOFeAs B_{VRH} > G_{VRH}; this implies that a parameter limiting the mechanical stability of this material is the shear modulus G_{VRH}.

The bulk modulus for LaOFeAs is rather small (at about 98 GPa), and is less than, for example, the bulk modules for other known superconducting species: MgB₂ (~ 122-161 GPa [34]), MgCNi₃ (~172-210 GPa [35]), YBCO (~ 200 GPa), and YNi₂B₂C (~200 GPa [3]). Thus, compared with other superconductors, LaOFeAs is the soft material.

According to criterion [36], the material is brittle if the B/G ratio is less than 1.75. In our case, for LaOFeAs B/G ~ 1.74, this suggests that this material lays at the border of a brittle behavior.

Finally, the values of the Poisson ratio (ν) for covalent materials are small (ν = 0.1), whereas for ionic materials a typical value of ν is 0.25 [37]. In our case the value of ν for LaOFeAs is at about 0.26, i.e. a higher ionic contribution in intra-atomic bonding for LaOFeAs phase should be assumed. Besides, for covalent and ionic materials, the typical relations between bulk and shear modulus are G ≃ 1.1B and G ≃ 0.6B, respectively. For our case the calculated value of G_V/B_V is 0.58, also indicating that the ionic bonding is suitable for LaOFeAs.

In summary, we have performed FLAPW-GGA calculations to obtain the elastic properties for mono- and polycrystalline oxyarsenide LaOFeAs as a basic phase for the newly discovered 26-52K superconductors. Our analysis shows that LaOFeAs belong to the anisotropic mechanically stable systems; a parameter limiting the mechanical stability of this material is the shear modulus. In addition, LaOFeAs is a soft material (B~98 GPa) with high compressibility (β ~ 0.0102 1/GPa); lays at the border of a brittle behavior and adopts a high ionic contribution in intra-atomic bonding.

-
- [1] Ming Lei, J. L. Sarrao, W. M. Visscher, T. M. Bell, D. J. Thompson, A. Migliori, U. W. Welp, and B. W. Veal, *Phys. Rev. B* 47, 6154 (1993).
- [2] J. E. Hirsch, *Phys. Rev. B* 55, 9007 (1997).
- [3] S. Meenakshi, V. Vijayakumar, R. S. Rao, B. K. Sikka, P. Ravindran, Z. Hossian, R. Nagarajan, L. C. Gupta, and R. Vijayathavan, *Phys. Rev. B* 58, 3377 (1998).
- [4] U. Jeanicke-Rossler, G. Zahn, P. Paufler, H. Bitterlich, and G. Behr, *Physica C* 305, 209 (1999).
- [5] H. Y. Wang, X. R. Chen, W. J. Zhu, and Y. Cheng, *Phys. Rev. B* 72, 172502 (2005).
- [6] I. R. Shein, V. V. Bannikov, and A. L. Ivanovskii, *Physica C* 468, 1 (2008).
- [7] N. Guclu, U. Koleman, O. Uzun, and S. Celebi, *Physica C* 433, 115 (2005).
- [8] E. A. Ekimov, V. A. Sidorov, E. D. Bauer, N. N. Melnik, N. J. Curro, J. D. Thompson, and S. M. Stishov, *Nature (London)* 428, 542 (2004).
- [9] Y. Takano, T. Takenouchi, S. Ishii, S. Ueda, T. Okutsu, I. Sakaguchi, H. Umezawa, H. Kawarada, and M. Tachiki, *Diamond Relat. Mater.* 16, 911 (2007).
- [10] R. M. Scanlan, A. P. Malozemoff, and D. C. Larbalestier, *Proc. IEEE*, 92, 1639 (2004).
- [11] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, *J. Am. Chem. Soc.* 130, 3296 (2008).
- [12] H. H. Wen, G. Mu, L. Fang, H. Yang, and X. Zhu, *cond-mat/0803.3021v1* (2008).
- [13] G. F. Chen, Z. Li, D. Wu, G. Li, W. Z. Hu, J. Dong, P. Zheng, J. L. Luo, and N. L. Wang, *cond-mat/0803.3790v1* (2008).
- [14] X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen and D. F. Fang, *cond-mat/0803.3603v1* (2008).
- [15] Z. A. Ren, J. Yang, W. Lu, W. Yi, G. C. Che, X. L. Dong, L. L. Sun, and Z. X. Zhao, *cond-mat/0803.4283v1* (2008).
- [16] Z. A. Ren, J. Yang, W. Lu, W. Yi, X. L. Shen, Z. C. Li, G. C. Che, X. L. Dong, L. L. Sun, F. Zhou, and Z. X. Zhao, *cond-mat/0803.4234v1* (2008).
- [17] I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, *cond-mat/0803.2740v1* (2008).
- [18] K. Kuroki, S. Onari, R. Arita, H. Usui, Y. Tanaka, H. Kontani, and H. Aoki, *cond-mat/0803.3325v1* (2008).
- [19] D. J. Singh, and M. H. Du, *cond-mat/0803.0429v1* (2008).
- [20] H. J. Zhang, G. Xu, X. Dai, and Z. Fang, *cond-mat/0803.4487v1* (2008).
- [21] C. Cao, P. J. Hirschfeld, and H. P. Cheng, *cond-mat/0803.3236v1* (2008).
- [22] H. Eschrig, *cond-mat/0804.0186v1* (2008).
- [23] G. F. Chen, Z. Li, D. Wu, J. Dong, G. Li, W. Z. Hu, P. Zheng, J. L. Luo, and N. L. Wang, *cond-mat/0803.4384v1* (2008).
- [24] F. Marsiglio, and J. E. Hirsch, *cond-mat/0804.0002v1* (2008).
- [25] H. W. Ou, J. F. Zhao, Y. Zhang, D. W. Shen, B. Zhou, L. X. Yang, C. He, F. Chen, M. Xu, T. Wu, X. H. Chen, Y. Chen, and D. L. Feng, *cond-mat/0803.4328v1* (2008).
- [26] W. Lu, J. Yang, X. L. Dong, Z. A. Ren, G. C. Che, and Z. X. Zhao, *cond-mat/0803.04234v1* (2008).
- [27] B. I. Zimmer, W. Jeitschko, J. H. Albering, R. Glaum, and M. Reehuis, *J. Alloys Compd.* 229, 238 (1995).
- [28] J. P. Perdew, S. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* 77, 3865 (1996).
- [29] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k, An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties*, (Vienna University of Technology, Vienna, 2001).
- [30] G. Xu, W. Ming, Y. Yao, X. Dai, S. C. Zhang, and Z. Fang, *cond-mat/0803.1282v1* (2008).
- [31] W. Voigt, *Lehrbuch der Kristallphysik*, Teubner, Leipzig, 1928.
- [32] A. Reuss, *Z. Angew. Math. Mech.* 9, 49 (1929).
- [33] R. Hill, *Proc. Phys. Soc. London, A* 65, 349 (1952).
- [34] A. K. M. A. Islam, F. N. Islam, M. S. Iqbal, A. F. Jalbout, and L. Adamowicz, *Solid State Commun.* 139, 315 (2006).
- [35] G. Vaitheeswaran, V. Kanchana, A. Svane, and A. Delin, *J. Phys.: Condens. Matter* 19, 326214 (2007).
- [36] S. F. Pugh, *Phil. Mag.* 45, 833 (1954).
- [37] J. Haines, J. M. Leger, and G. Bocquillon, *Ann. Rev. Mater. Res.* 31, 1 (2001).